

# **Characterization of Corrosion Products and Microbes on Various Types of Metal Coupons Using Beamline 1.4.3**

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Microbes primarily exist in complex consortia (biofilms) of interacting physiological groups in the environment. This presents a complex problem for microbiologists attempting to assay samples for microbial biomass, viable count, etc. because one cannot always grow what is present (there is no universal medium guaranteed to do that), and it is difficult, if not impossible to quantitatively remove all the bacteria from the surfaces to which they are attached, as well as from one another. FTIR spectroscopy is suitable for fundamental biofilm research, as well as for monitoring biofilm formation on surfaces, including reflecting surfaces like metals, which become especially corroded in the presence of natural waters and industrial service waters containing microorganisms. It is also capable of allowing microorganisms present in a sample to be identified and so presents a new addition to taxonomic and genetic methods already in use. The FTIR analysis of bacterial isolates provides fingerprint spectra, which facilitates the rapid characterization of microbial strains. The analytical discrimination between microorganisms, inorganic material or other foulants (such as corrosion products) can be obtained nondestructively, in situ, and in real time.

IR spectroscopy has been used to identify microorganisms for over 40 years, based on the observation that different bacteria display different IR spectra. However, bacterial cells, especially when organized into a biofilm, represent an extremely complex system. Many different signals arise from vibrations of molecules in the extracellular polymeric substances, the cell wall, the cell membrane and the cytoplasm. This leads to overlapping and broadening of bands in the spectra, which cannot be completely separated. Nonetheless, the mid-IR region (4000 to 500  $\text{cm}^{-1}$ ) contains a variety of characteristic marker bands relevant to the identification of microorganisms. In addition, mathematical and statistical methods have been developed that allow further analysis of spectral information and a spectral library has been established.

Since most structural and functional groups of different bacteria are identical and give essentially the same signals, how can bacterial spectra be distinguished? The answer lies in the fact that the quantity and distribution of these functional groups vary among microbial strains. These differences are hardly noticeable when looking at the original FTIR spectra, but can be more easily distinguished by calculating and comparing the second derivative spectra.

The goal of this research is to characterize and locate deterioration products and bacteria associated with corrosion occurring on small metal coupons removed from experimental sidestreams associated with the service water systems at various power plants located throughout the US. FTIR spectromicroscopy is a perfect tool for this kind of investigation, and the high-quality signal from a small beam size generated by the synchrotron source is necessary for the high-resolution mapping necessary for this project.

Four types of metal coupons (mild steel, admiralty brass, stainless steel and copper) were inserted into a sidestream attached to the chilled water system at UC Irvine as part of an ongoing investigation of corrosion in industrial water systems. Metal coupons were removed after 10 months in the test loop, stained with fluorescent dyes that bind to DNA, and viewed for the presence of biofilm bacteria using a confocal scanning laser microscope (CSLM). Duplicate coupons were shipped overnight to LBNL and viewed the next day using the FTIR spectromicroscope at ALS beamline 1.4.3. The basic principle of detection of bacterial biofilms on a surface is to search for marker bands diagnostic for the presence of bacteria such as protein and polysaccharide IR bands. The characteristic Amide I and II bands are significant and can be found in all spectra derived from bacterial samples, indicating the presence of a biological fouling layer (biofilm). Results from sampling the coupons indicate the presence of bacterial microcolonies on all of the coupons, in agreement with the staining results seen with CSLM. FTIR spectra from three visually different regions on a copper coupon are presented below. These spectra indicate a variety of peaks, especially in the "fingerprint" region of the spectrum (below 1500  $\text{cm}^{-1}$ ), significant for deformation, bending, and ring vibrations which can be very specific for a substance or for different types of substitution.

Future research will call for removing metal coupons from the test loops at various times after insertion in order to determine how quickly bacteria attach to form microcolonies or biofilms on the coupons, as well as to determine when and where the first corrosion products build up on the surface. In addition, the corrosion products and resident bacteria will be characterized as much as possible. To date most research has indicated that sulfate-reducing bacteria are the major cause of microbiologically influenced corrosion (MIC). Yet there is ample evidence to suggest

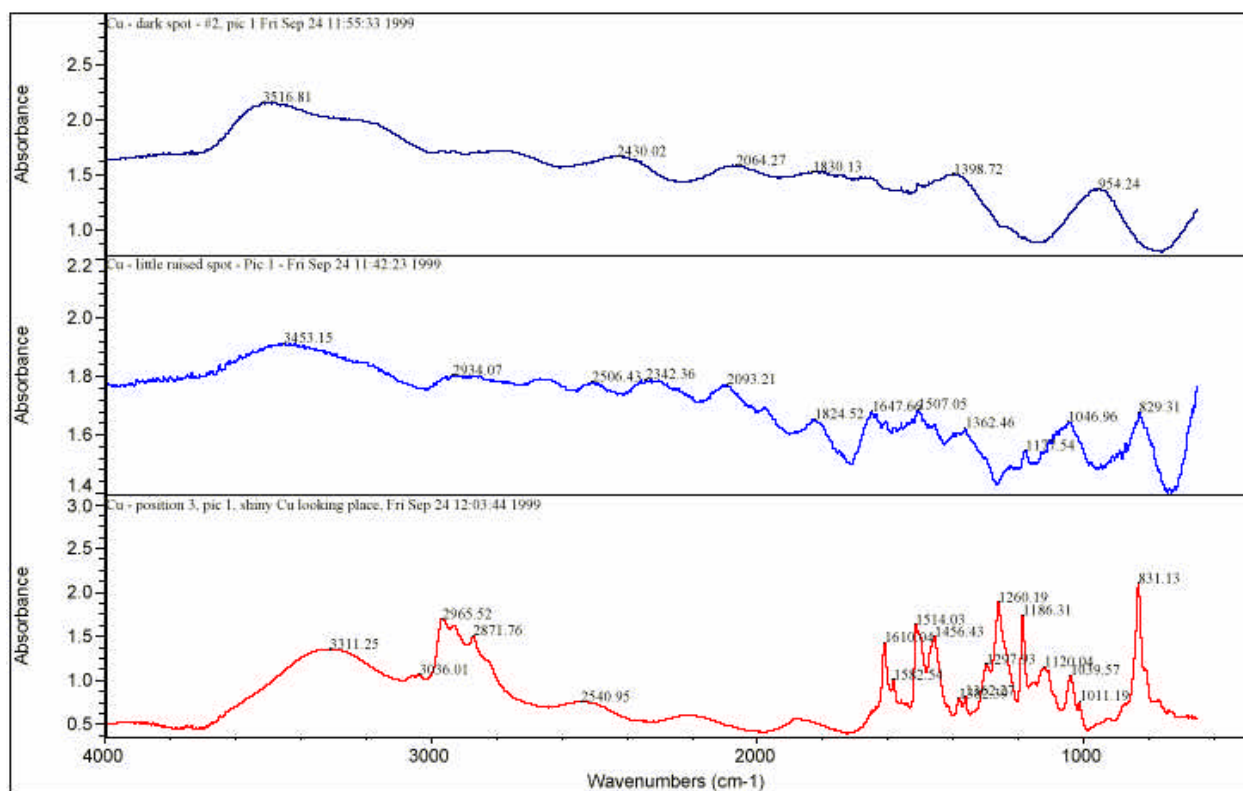


Figure 1. FTIR spectra from visually different locations on a copper coupon that had spent 10 months in the Central Generating Facility's service water sidestream, UC Irvine.

that other types of bacteria (iron and manganese oxidizing and reducing bacteria, for example) may also play a role in MIC. We want to investigate the microbial ecology of the coupons in order to gain insight into the localization and real-time mechanisms for production of corrosion products on the metal surface. After FTIR mapping, the metals will be treated (using standard ASTM procedures) to remove all the materials fouling the surface and then examined for pitting and other corrosion damage. The positions of these damage sites can then be compared to the chemical and biological information gained from the FTIR spectromicroscopy studies.

Transportable corrosion test units have been designed and built with input from several corrosion experts. These units are located at UC Irvine (in the Central Generating Facility) and at the Three Mile Island nuclear plant. We are currently making arrangements to have additional units installed at several other power plants within the next several months. Coupon samples from these studies will be removed from each of the test systems and investigated at the ALS. In addition, a corrosion test system has been constructed in the laboratory at UC Irvine; this system allows us to vary the experimental parameters (flow rate, temperature, addition of biocides or anticorrosive agents, etc.) in a way not possible with the units in the field.

In summary, this ongoing research is expected to add to a greater understanding of the complex abiotic and biotic factors affecting the corrosion of metals, which each year costs industries and governments billions of dollars worldwide.

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